

Ground state of antiferromagnetic ordering in fullerene C_{60} molecule

C.V. Usenko¹

V.C. Usenko²

¹ *Taras Shevchenko Kiev University, Physical Department. 6, Academician Glushkov pr., Kiev 03127, Ukraine*

² *Institute of Physics, NAS of Ukraine. 46, Nauky pr., Kiev 03022, Ukraine*
(February 1, 2008)

Theoretical study of mutual orientation of fullerene C_{60} molecule atom spins is presented in this work. Spin-spin interaction was described by Hubbard's model. Existence of antiferromagnetic structure of spin sub-system in ground state is found. It is also shown that spin distribution practically does not depend on weak anisotropy due to Jan-Teller effect.

I. INTRODUCTION

At theoretical study of a fullerene molecule C_{60} , general approach is to use the localized electrons model [3] [7]. Though question on if in fullerene there exists an ordered spin subsystem was practically not considered. In general, study of magnetic properties of a fullerene molecule C_{60} is now at the very beginning. Theoretical works by Gunnarson et al., in particular, "Mott-Hubbard insulators for systems with orbital degeneracy" [1], where application of Hubbard model to simplest lattices with space topology close enough to topology of fullerenes, in particular, tetragon and triangle, is considered, are known. Authors of that work have practically approached the problem of study of doped fullerenes magnetic properties. Recently an experimental work by Schilder et al. [6], "The role of TDAE for the magnetism in C_{60} ", appeared as well, where magnetic properties of a doped fullerene are studied, in particular - effect of admixture on those properties. In this work theoretical aspects of fullerene C_{60} magnetic properties are studied, it is proved that there exists a ground state of fullerene molecule spin subsystem; properties of the ground state are proved to be practically independent from the binding in fullerene molecule anisotropy.

In the case of anti-ferromagnetism all or some of magnetic moments of atoms are oriented in such a way (usually those are anti-parallel) that total magnetic moment of crystal unit cell is zero (or is a small part of moment of an atom). Here anti-ferromagnetism differs from ferromagnetism, in the case of which same orientation of all atomic magnetic moments leads to high magnetization of the body. Responsible for anti-ferromagnetism coming to existence is exchange interaction, that is trying to arrange spins (and, thus magnetic moments) in anti-parallel way; in such a case exchange integral has a negative value. Type of magnetic ordering is determined by magnetic atomic structure, symmetry of which is described by point and space groups of magnetic symmetry. Unit cell of magnetic structure may coincide with crystallographic one, or it can be multiple of it (for instant, have a twice larger period). Magnetic structure of anti-ferromagnets is described by a set of embedded magnetic sub-lattices, each with magnetization \vec{M}_j . In all anti-ferromagnets, except of those with weak ferromagnetism, under absence of external magnetic field, $\sum_j \vec{M}_j = 0$. In the case of magnetic sub-lattices application one considers for anti-ferromagnets properties description (in particular, to describe transition from paramagnetic state to anti-ferromagnetic one) following parameters: vector of anti-ferromagnetism $\vec{L} = \vec{M}_1 - \vec{M}_2$ and vector of magnetization $\vec{M} = \vec{M}_1 + \vec{M}_2$ (for two sub-lattices).

The term "magnetic sub-lattice" came into existence when number of sub-lattices for known crystals did not exceed two, i. e. when for magnetic structures of crystals only the simplest ones were known: ferromagnetic structure (one sub-lattice) and collinear anti-ferromagnetic (two sub-lattices, later on Neel's collinear ferromagnetic structure being added, having in simplest cases two sub-lattices as well). Later on magnetics with more complicated, non-collinear magnetic structures have been found, having, respectively, a larger number of sub-lattices (three, four and more). Obviously, number of sub-lattices can not exceed number of atoms in a magnetic cell. Properties of ferromagnets with multiple sub-lattices, in particular, effects like sub-lattices overturn (jump turn of atomic magnetic moments at external magnetic field, applied along the axis of symmetry, coming to some critical value, related to anisotropy of magnetic susceptibility), relativistic distortion of sub-lattices mutual orientation, are studied in works by Marchenko et al. [3,4].

In wide-spread carbon compounds, like graphite and diamond, it is not possible to isolate the spin state of one atom, because of collectivization of valence electrons (this results from strong interatomic interaction and crystalline

structure of such substances). One of consequences is that those matters do not show magnetic properties. Another situation one finds for the fullerene molecule C_{60} , where number of atoms is much less than in the case of diamond or graphite and this makes it possible to suppose all electrons to be localized on atoms. For molecules of such a type one should expect existence of some order in atomic spins orientation, and this can influence magnetic properties. Since interaction of p-electrons spins seeks to turn spins of neighbouring atoms in opposite directions, anti-ferromagnetism should be specific for C_{60} molecules.

In accordance to Hund's rule, the lowest energy is specific for the term with the maximal possible at given electronic configuration value of the total spin of electrons S and the largest (possible at that S) value of total orbital moment L . Thus, if spin of an atom (being, really, the sum of spins of electrons in outer shell) is non-zero, it, in accordance to Hund's rule, takes the maximal value. Average spin of an atom is a part of the total moment of momentum of the valence electrons system, and its value depends on electronic configuration. For a separate carbon atom configuration s^2p^2 is specific, where spins of s -electrons have opposite orientation, though for the same atom in chemical compounds, in fullerene among those, configuration sp^3 is more often, where all electron spins, in accordance to Hund's rule, are parallel, and total atomic spin is to equal 2.

Intrinsic magnetic moment of an atom, thus moment without external field, is:

$$\vec{\mu}_o = -\mu_B(\vec{L} + 2\vec{S}) \quad (1)$$

where μ_B is the Bohr magneton, \vec{L} - total orbital moment of an atom, \vec{S} - total spin of an atom. In a carbon atom of a fullerene molecule orbital moments of all electrons are compensated, thus total orbital moment is $\vec{L} = 0$. Hence, intrinsic magnetic moment of each atom is collinear to its spin vector. Thus, to disclose carbon atoms in molecule C_{60} configuration it is enough to determine configuration of atomic spins of the molecule, thus the spin (or, this is the same, anti-ferromagnetic) ordering; question on localization and configuration of spins is, hence, closely related to magnetic properties of a molecule. In the study of spin ordering account of carbon atoms spin - spin interaction, determining, in fact, configuration, is needed. Main state of ordering is in such a case the one with minimal energy of spin interaction.

II. PROBLEM FORMULATION

Neglecting spin-spin interaction, one can consider in zero approximation spins of different atoms to be independent, and in first-order approximation interaction of those is determined by Heizenberg's Hamiltonian,

$$H_H = \frac{1}{2} \sum_{i \neq j} J_{i,j} \hat{S}_i \cdot \hat{S}_j \quad (2)$$

Interaction of spins is determined by the overlap integrals for coordinate wave functions of valence electrons

$$J_{i,j} = \langle \varphi_i | \varphi_j \rangle \quad (3)$$

In first-order approximation one can take into account interaction of first neighbors only, neglecting wave functions overlapping for all other pairs of atoms. In C_{60} molecule each atom has three nearest neighbors, similar to diamond or graphite, thus in interaction energy inputs of only three nearest atoms are left:

$$\langle H_H \rangle = \frac{1}{2} \sum_i \left(J_1 \langle \vec{S}_i \rangle \cdot \langle \vec{S}_{i1} \rangle + J_2 \langle \vec{S}_i \rangle \cdot \langle \vec{S}_{i2} \rangle + J_3 \langle \vec{S}_i \rangle \cdot \langle \vec{S}_{i3} \rangle \right) \quad (4)$$

It is taken into account here that because of symmetry overlap integrals with respective neighbor for each atom coincide, and indices $i1, i2, i3$ stand for number of respective neighboring atom. Jan-Teller effect removes, in a part, degeneration of values for overlap integrals, though difference in distances between atoms (1.45, 1.45 and 1.40) is small enough to neglect it in model approximation.

$$\langle H_H \rangle = \frac{1}{2} J \sum_i \left(\langle \vec{S}_i \rangle \cdot \langle \vec{S}_{i1} \rangle + \langle \vec{S}_i \rangle \cdot \langle \vec{S}_{i2} \rangle + \langle \vec{S}_i \rangle \cdot \langle \vec{S}_{i3} \rangle \right) \quad (5)$$

Sign of overlap integrals defines the properties - either ferromagnetic, or paramagnetic - to take place. For carbon overlap integral is positive, thus parallel spins would correspond to maximum in the spin-spin interaction energy, while minimal energy is to be observed for absolutely antiparallel spins. As it was mentioned above, surface of the

C_{60} molecule is arranged of pentagons and hexagons, with carbon atoms in vertices. Before considering molecule as a whole we find configurations of atomic spins for atoms in vertices of two such polygons, under condition of antiparallel orientation of spins (this condition follows from requirement for minimum of energy of interaction between spins). In the case of hexagon there are no problems with arrangement - antiparallel orientation for each two nearest neighbors completely satisfies this criterion. Though in case of pentagon situation is more complicated. Because of number of vertices being in this case uneven, it is not possible to arrange for such a figure a really antiparallel system of spins, orthogonal to its plane. Thus it turns out that it is not possible to arrange for a fullerene a usual anti-ferromagnetic ordering, with two magnetic lattices; in reality more are needed. These considerations make evident that orientation of spins in a fullerene molecule shall be of such a type that makes energy of spin-spin interaction minimal for the molecule as a whole only, and not for each pair of neighboring atoms. Such a minimum for a molecule as a whole is possible in the case of long-range atomic spins ordering only, i. e. under condition of totally correlated spin directions for not only nearest neighbors, but all atoms in the molecule as well. Aim of this work is to find such an arrangement.

Problem on atomic spins interaction for a C_{60} molecule in the model of localized electrons is studied under following assumptions:

- Only spin-spin interaction for nearest neighbors (three of those for each atom) is taken into account;
- Constants of interaction are considered as being same for each pair of atoms (Jan-Teller effect is neglected);
- Possible changes in average values of spins for each atom are neglected (semi-classical approach).

Complexity of the problem in comparison to anti-ferromagnetic crystals models is in absence of long-range ordering, leading to necessity of studying spins for all 60 atoms simultaneously. Space orientation of spins is determined by 2×60 angles, or 3×60 unit vector components. Since symmetry group of C_{60} molecule is simple, possibility to isolate sub-lattices with same arrangement of spins does not exist. Specific structure of neighbors arrangement for each atom does not allow to use same notation for the system of neighbors, and makes it again necessary to study spins of all atoms. With account of all approximations, one can represent the spin-spin energy of interaction in C_{60} molecule as

$$E = \frac{JS^2}{2} \sum_{i=1..60} \sum_{k_i=1_i,2_i,3_i} \vec{n}_i \cdot \vec{n}_{k_i} \quad (6)$$

Here it is taken into account that spin of each atom can vary in direction only, thus for the i th atom "i" spin we use notation

$$\vec{S}_i = S\vec{n}_i, \quad (7)$$

where vector of direction of the spin \vec{n}_i is a unit vector, and indices $1_i, 2_i, 3_i$ stand for neighbors of i th atom. Thus problem is in finding the minimum of spin-spin interaction energy (6) under condition of preserving lengths of all vectors \vec{n}_i , which imposes an additional condition

$$|\vec{n}_i|^2 = 1; i = 1..60. \quad (8)$$

It is easy enough to determine the lower limit of minimal energy: for each separate node minimal energy would be observed in the case of spins of all neighboring atoms being arranged in parallel to each other and in antiparallel orientation with respect to spin of that node. In such a case each scalar product for that node is -1, and if it was possible to arrange all the spins in such a way, total energy would be

$$E_{hyp. \min} = -90JS^2. \quad (9)$$

In reality, because of specific topology, it is not possible to arrange all spins of the C_{60} molecule in antiparallel way, thus energy of spin-spin interaction, even for ground state, exceeds this value.

Consider first a much simpler, as from point of view of number of atoms, though a topologically similar imaginary molecule, formed by 4 atoms, situated in vertices of a regular tetrahedron. Spin-spin interaction energy can be represented in explicit form:

$$E_{ss} = JS^2 (\vec{n}_1 \cdot \vec{n}_2 + \vec{n}_1 \cdot \vec{n}_3 + \vec{n}_1 \cdot \vec{n}_4 + \vec{n}_2 \cdot \vec{n}_3 + \vec{n}_2 \cdot \vec{n}_4 + \vec{n}_3 \cdot \vec{n}_4). \quad (10)$$

If each couple of spins was antiparallel, energy of such a state would be

$$E_{hyp. \min} = -6JS^2. \quad (11)$$

Symmetry considerations make it possible to find out that minimum is observed with all the spins oriented in direction from the center of tetrahedron, or towards its center. Each scalar product equals $-\frac{1}{3}$, and sum of those $-E_{ss} = -2JS^2$, this is three times larger than the lower limit estimation mentioned above.

This example makes evident that there is a conventional possibility to consider the state with minimal energy as being equilibrium only. Substantial peculiarity of tetrahedron model is in fact that angles formed by directions from the molecule center to each node exceed in this case the right ones, thus even in the most symmetric state main energy, falling for each state, is negative. Even for the next in complexity model, a cube, such a radial spins arrangement can provide not more than a zero value of energy of interaction with nearest neighbors. For more complicated molecules, with C_{60} among those, angles between spins at radial arrangement tend to zero, thus energy of spin-spin interaction for such an arrangement shall tend to absolute maximum. In fact, this means that if for a tetrahedron radial arrangement of spins is optimal (thus it corresponds to minimal energy), similar radial arrangement in the case of fullerene shall lead to opposite result.

III. SPIN SUB-SYSTEM GROUND STATE

Equations of motion for the spin system have steady-state solutions only in the case of sum of spins of nearest neighbors of each atom having parallel to that atom's spin orientation. Really, if one rewrites the system of equations of motion as follows:

$$\frac{d\vec{n}_i}{dt} = JS^2\vec{n}_i \times \sum_{j \neq i} \vec{n}_j, \quad (12)$$

it is easy to see that under condition

$$\sum_{k_i} \vec{n}_{k_i} = \lambda_i \vec{n}_i \quad (13)$$

all spins are in rest, and energy of spin-spin interaction equals

$$E_{ss} = JS^2 \sum_{i=1..60} \lambda_i. \quad (14)$$

The lowest of all possible values of the sum of parameters λ_i corresponds to the state with minimal energy. With account of symmetry of the molecule it is possible to consider λ_i as being the same for all the nodes. Besides that, all vectors \vec{n}_i are to be of the same (unit) length, thus one has to add to the system (13) conditions being imposed on the vector lengths

$$|\vec{n}_i|^2 = 1; i = 1..60. \quad (15)$$

Those conditions make the problem to be non-linear.

System of equations (13) can be divided into three similar systems

$$\begin{aligned} \sum_{k_i} n_{xk_i} &= \lambda_i n_{xi} \\ \sum_{k_i} n_{yk_i} &= \lambda_i n_{yi} \\ \sum_{k_i} n_{zk_i} &= \lambda_i n_{zi} \end{aligned} \quad (16)$$

Input data are coordinates of atoms of fullerene molecules. All calculations have been done in the program package Maple V.5 by means of a system of analytic calculations, being a part of the package. Each step of solving the problem was implemented as a separate program. To solve the problem following algorithm is used:

1. Atoms of the fullerene molecule are sequentially numbered. For each atom numbers of three nearest neighbors are found. Next, a matrix 60×60 is arranged, where in each line there are values "1" in elements, numbers of which coincide with numbers of nearest neighbors of the atom corresponding to number of line, all other elements have values "0". It is obvious that since approximation of three nearest neighbors is considered, in different positions of each line there are three values "1". This matrix (let it be L) is the matrix of the system of equations (16).

2. Next, eigenvalues and eigenvectors of matrix L are found. Minimum eigenvalue λ_{\min} , corresponding to the state of spin subsystem with minimal ordering energy, is of triple degeneracy. As one should expect, respective eigenvectors (60 components each) form the set of coordinates \vec{n}_i for the problem.
3. While the study it turned out that eigenvectors found are not orthonormal ones, i. e. coordinates of vectors \vec{n}_i were found not in orthogonal basis. Orthonormalization of eigenvectors was performed.
4. By components of orthonormal eigenvectors of matrix L vectors \vec{n}_i of spin directions for each node are constructed. Checkup of vector lengths congruence is performed.
5. By respective minimal eigenvalue of matrix L energy of ground state of the spin sub-system ordering is found. Last, graphic representation of a fullerene molecule and atomic spins vectors in eigenvalue is performed.

IV. RESULTS

The minimum eigenvalue found

$$\lambda_0 = -2.6180,$$

as it is mentioned above, has triple degeneration, and a set of respective orthonormal eigenvalues that satisfies conditions of normalization is found, thus the problem on the ground state of spin sub-system has been solved. Energy corresponding to minimal eigenvalue is

$$E_{ss} = 60JS^2\lambda_0,$$

this is a little (by 13%) higher than minimum. Following picture 1 shows the C_{60} molecule, with directions of spins of all the atoms.

FIG. 1. Directions of spins.

V. CONCLUSIONS

Results obtained in this study make evidence of stationary states for the fullerene molecule spin subsystem ordering existence in localized spin model. Value of energy for the spin sub-system ground state is a bit higher than theoretically possible minimum. The spin sub-system spectrum practically does not depend on weak anisotropy due to Jan-Teller effect.

-
- [1] Golod P. I., Loktev V. M. // UFJ.-1992.-V. 37, N 6.-P. 818-823 (Ukrainian)
 - [2] Eletsky A. V., Smirnov A. V. Fullerenes. // UFN-1993.-V.. 163, N 2.-P. 33-59 (Russian)
 - [3] Gunnarson O., Koch E., Martin R.M. // Max-Planck-Institute. Jan. 1999
 - [4] Marchenko V. I., Tikhonov A. M. // Pisma v JETP.-1999.-V.69, no. 1.-P. 41-45
 - [5] Marchenko V. I., Tikhonov A. M. // Pisma v JETP.-1999.-V.68, no. 11.-P. 844-846
 - [6] Schilder A., Bietsch W., Schwoerer M. // New Journal of Physics. 1999. V. 1. P. 5.1-5.11
 - [7] Aryasetiawan F., Gunnarson O., Koch E., Martin R.M. // Max-Planck-Institute. Jan. 1999
 - [8] Kratschmer W., Fostiropoulos K., Huffman D.R. // Chem. Phys. Let. 1990. V. 170. P. 167

